Modelling the bioaccumulation of persistent organic pollutants in agricultural food chains for regulatory exposure assessment

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Chapter 4 - Modelling the bioaccumulation of persistent organic pollutants in agricultural food chains for regulatory exposure assessment

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4-1 Abstract

New models for estimating bioaccumulation of persistent organic pollutants in the agricultural food chain were developed using recent improvements to plant uptake and cattle transfer models. One model named AgriSim was based on K_{OW}-regressions of bioaccumulation in plants and cattle, while the other was a steady-state mechanistic model, AgriCom. The two developed models and EUSES, as a benchmark, were applied to four reported food chain (soil/air-grass-cow-milk) scenarios to evaluate the performance of each model simulation against the observed data. The four scenarios considered were: (1) polluted soil and air, (2) polluted soil, (3) highly polluted soil surface and polluted sub-surface, (4) polluted soil and air at different mountain elevations. AgriCom reproduced observed milk bioaccumulation well for all four scenarios, as did AgriSim for Scenarios 1 and 2, but EUSES only did this for Scenario 1. The main causes of the deviation for EUSES and AgriSim were the lack of the soil-air-plant pathway and the ambient air-plant pathway respectively. Based on the results, it is recommended that soil-air-plant and ambient air-plant pathway should be calculated separately and the K_{OW} regression of transfer factor to milk used in EUSES be avoided. AgriCom satisfied the recommendations that led to the low residual errors between the simulated and the observed bioaccumulation in agricultural food chain for the four scenarios considered. It is therefore recommended that this model should be incorporated into regulatory exposure assessment tools. The model uncertainty of the three models should be noted since the simulated concentration in milk from 5^{th} to 95^{th} percentile of the uncertainty analysis often varied over two orders of magnitude. Using a measured value of soil organic carbon content was effective to reduce this uncertainty by one order of magnitude.

4-2 Introduction

The bioaccumulation of persistent organic pollutants in agricultural food chains is a process in which pollutants are transferred from contaminated sources, such as ambient air and soil to agricultural products, such as crops and beef and dairy products, and then to humans. Modelling and simulation techniques for processes such as plant uptake and cattle transfer have been developed (Travis and Arms 1988; Trapp and Matthies 1995) and these models have been incorporated into regulatory exposure assessment tools (Arnot and Mackay 2008; Lijzen and Rikken 2004; Mckone 1993).

The European Union System for the Evaluation of Substances (EUSES) is one of the regulatory assessment tools, based on the European Commission Technical Guidance Documents on Risk Assessment (TGD) (Lijzen and Rikken 2004; European Commission, 2003). EUSES has an agricultural food chain component, which is composed of the uptake of pollutants into root and leafy crops, and grass derived from Trapp and Matthies (1995) model, and their subsequent transfer into cow's milk and beef derived from Travis and Arms (1988) model. While EUSES is routinely used by regulatory authorities in the EU and elsewhere (ECHA 2011; VKM 2009; Elert, 2008), the accuracy of this model to predict contamination of the agricultural food chain has been questioned. For example, the root model, the empirical equation of transpiration stream concentration factor and of cattle biotransfer in EUSES have shown significant deviations from newly derived observed data (Undeman and McLachlan 2011; McKone and Ryan 1989; Birak et al. 2001).

Recently, the performance of plant uptake and cattle transfer models which form significant parts of these exposure assessment tools were evaluated (Takaki et al. 2014; Takaki et al. 2015). When agricultural soil was contaminated, the model simulations of both plant uptake and cattle transfer in EUSES did not reproduce the observed uptake and transfers. The main causes of the poor simulations were the wrong selection of a parameter value, i.e., root lipid to octanol correction exponent, the omission of the soil-air-plant pathway, and the low accuracy of K_{OW}-regressions for cattle transfer of pollutants. However, some improvements in each model were able to be demonstrated through: the careful selection of the transpiration and volatilisation parameters in the plant uptake model in reference to the original document (Trapp and Matthies 1995; Jury et al. 1983), and the use of Quantitative Structure-Activity Relationship (QSAR) biodegradation models for estimating the metabolic rate of cattle (Takaki et al. 2014; Takaki et al. 2015).

The aim of this study was to integrate the previously improved plant uptake and cattle transfer models to build an integrated model for simulating agricultural food chain bioaccumulation of organic pollutants for the purpose of regulatory exposure assessments. The integrated model performance was evaluated with four different scenarios from the reported experimental observation which considered a food chain, soil/air-grass-cow-milk. The performance of EUSES, the widely used existing tool, was also assessed as a benchmark with which to compare the performance of the integrated model.

4-3 METHODS

Two models for simulating agricultural food chain bioaccumulation of persistent organic pollutants were developed: a simple model, AgriSim and a complex model, AgriCom. The agricultural food chain component of EUSES was also used. The structures of each model are shown in Figure 4-1 and the model equations are described in APPENDIX V. To provide real-world data for comparative purposes, four different examples dealing the contamination of milk with persistent organic pollutants from contaminated soil and air were chosen from the literature (McLachlan 1996; Mamontova et al. 2007; Batterman et al. 2009; Shunthirasingham et al. 2013).

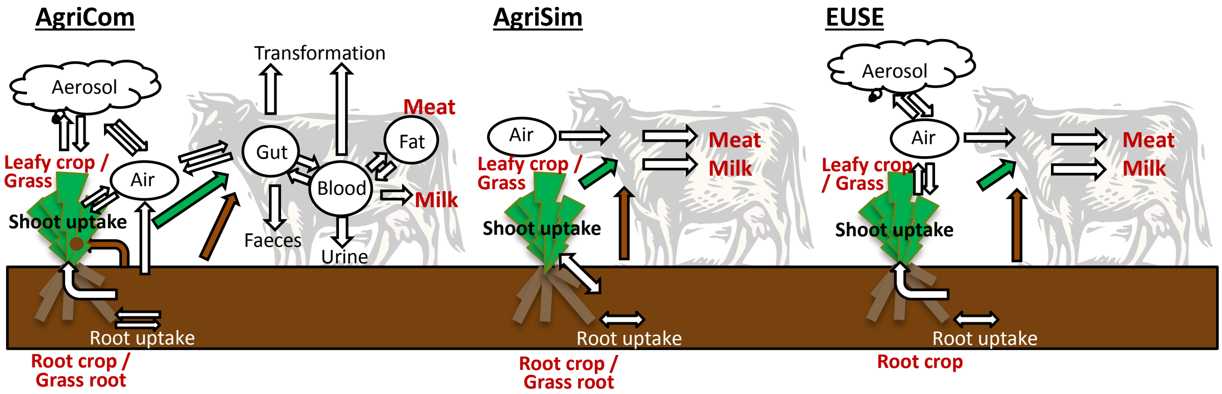


Figure 4-1 The overall structures of agricultural food chain bioaccumulation models developed and tested in this study (AgriCom and AgriSim) and EUSES, which is tested and compared in this study. Double headed arrows mean that equilibrium is assumed.

4-3-1 Model Descriptions.

Root uptake

The root uptake models of AgriSim and EUSES were derived from the Trapp and Matthies (1995) model, which simulates the root-pore water equilibrium. AgriCom used dynamic steady-state root uptake model by Trapp (2002) because the theoretical weakness of the equilibrium assumption was previously highlighted (Trapp and Schwartz 2000; Takaki et al. 2014). EUSES was demonstrated to have an inappropriate default parameter value for the octanol-root lipids correction factor, leading to poor estimation of root uptake (Takaki et al. 2014). AgriSim uses the default parameter values of CSOIL model (Brand et al. 2007), which demonstrated the best performance of all the five root uptake models during testing (Takaki et al. 2014). AgriCom included the parameter of growth dilution into the Trapp and Matthies (1995) model for the theoretical reinforcement. The value of growth dilution was optimised to minimise the residual errors between the modelled and the observed root uptake (see APPENDIX V).

Shoot uptake

AgriSim simulated the shoot uptake based on an empirical equation of the stem concentration factor proposed by Ryan et al. (1988) and incorporated in the CLEA model(Jeffries and Martin 2009). However, the maximum value of transpiration stream concentration factor by Briggs et al. (1982) and Hsu et al. (1990) was adopted to improve the model performance(Takaki et al. 2014). AgriCom and EUSES incorporated the Trapp and Matthies (1995) model which consists of two pathways: soil-root-shoot and air-shoot. AgriCom incorporates another three pathways: soil-air-shoot, soil particle-shoot, and aerosol-shoot. The soil-air-shoot and soil particle-shoot pathways of AgriCom were based on the representation used in the CSOIL model(Brand et al. 2007) and parameterised using the method of Takaki et al. (2014). The aerosol-shoot pathway was also added(Legind and Trapp 2009) because of its importance for chemicals with $\log K_{OA} > 11$, e.g., Heavily chlorinated PCDD/Fs (McLachlan 1999).

Cattle transfer

EUSES uses the K_{OW}-regression equation developed by Travis and Arms (1988) for estimating cattle transfer to milk and beef. However, the transfer is more significantly affected by the metabolism of individual chemicals in cattle rather than their hydrophobicity particularly in the K_{OW} range of 10^3-10^6 (Staple et al. 1997; Hendriks et al. 2007). The metabolic rate in cattle was found to be predicted well by the combination of QSAR biodegradation models of microorganisms (BioWIN (Boethling et al. 1994)), and fish (EPI-HL (Arnot et al. 2009), and IFS-HL (Brown et al. 2012)), that is, the biodegradation by microorganisms mimics the metabolic process in cattle gut, and the biodegradation by fish mimics metabolism after the absorption, which mainly occurs in the liver (Takaki et al. 2015). For estimating the cattle transfer to milk and beef, AgriSim incorporated the regression models between the biotransfer factor and the metabolic rate predicted by the QSARs and AgriCom adopted a mechanistic model based on CKow model (Rosenbaum et al. 2009) and the metabolic rate predicted by the QSARs, both of which showed the highest performance in the model comparison(Takaki et al. 2015).

The Procedural Models

AgriSim and AgriCom, were coded in Excel©. As for EUSES, the equations used in this study were coded into a new spread sheet. The chemical properties considered, such as K_{OW}, K_{OC}, and the Henry's law constant were taken from EPI Suite™ (US EPA 2012) except the K_{OW} values of PCBs, and PCDD/Fs, which were derived from specific studies by Schenker et al. (2005), and Chen et al. (2001) respectively. The concentration in milk of each pollutant derived from cattle raised on contaminated soil and surrounding air was then calculated and compared with experimental results from the literature. In addition, the contribution of each pathway for the contamination in milk (%) was calculated. An overview of the models and data requirements is provided in Table 4-1, and the model equations are described in APPENDIX V.

TABLE 4-1. Summary of data requirements and descriptions of Models Used in This Study.

Models		AgriCom	AgriSim	EUSES (EC-TGD)
Chemical properties needed		K_{OW}, H, MW, VP_L, K_{OC}, BioWIN4 score, EPI-HL, IFS-HL	K_{OW}, H, K_{OC}, BioWIN4 score, EPI-HL, IFS-HL	K_{OW}, H, S, VP_L, K_{OC}
Minimum requirement for the simulation		Chemical structure (SMILES) Concentration in soil or air	Chemical structure (SMILES) Concentration in soil or air	Chemical structure (SMILES) Concentration in soil or air
External tools needed		EPI-Suite™, IFS-HL	EPI-Suite™, IFS-HL	EPI-Suite™
Plant uptake pathways considered		Soil-Root Soil-Xylem-Shoot Soil-Air-(Aerosol)-Shoot Air-(Aerosol)-Shoot Soil particle-Shoot	Soil-Root Soil-Xylem-Shoot	Soil-Root Soil-Xylem-Shoot Air-Shoot
Type and time scales	Root uptake	mechanistic / empirical steady state	empirical equilibrium	empirical equilibrium
	Shoot uptake	mechanistic / empirical steady state	empirical equilibrium	mechanistic / empirical steady state
	Cattle transfer	mechanistic / empirical steady state	empirical (regression)	empirical (regression)
References		(Trapp, 2002; Trapp & Matthies, 1995; Takaki et al., 2014; Rosenbaum et al., 2009; Takaki et al., 2015)	(Brand et al., 2007; Ryan et al., 1988; Jeffries & Martin, 2009; Takaki et al., 2014; Takaki et al., 2015)	(Trapp & Matthies, 1995; Lijzen & Rikken, 2004; Travis & Arms, 1988)

K_{OW}: octanol-water partition coefficient, H: Henry law constant, MW: molecular weight, VP_L: vapour pressure for pure product, K_{OC}: organic carbon-water partition coefficient, BioWIN4 score: the output of BioWIN4 model, EPI-HL and IFS-HL: half life as the output of EPI-HL and IFS-HL model respectively.

4-3-2 Experimental Descriptions and Coverage of the Four Data Scenarios.

Contamination with hydrophobic pollutants from polluted soil and air

This study uses a field-based data set for chemical concentrations in air, aerosol, soil, grass, corn, and cow's milk in southern Germany that was collected from six sources by McLachlan (1996) and includes: McLachlan et al.(1992); McLachlan unpublished work; McLachlan (1992); McLachlan et al. (1994); Welsch-Pausch et al. (1995); Lassek et al. (1993). The targeted compounds were hydrophobic pollutants such as HCB, PCBs, and PCDD/Fs. Although the data for each media was not collected from the same place at the same time and the data contained an unpublished work unlike the other three scenarios, the concentration of three contamination sources, soil, air, aerosol, were available. The fugacity analysis indicated that the soil and the air were close to equilibrium for the pollutants (McLachlan 1996). All the three contaminated sources were used for input into AgriCom, the concentration in soil and air into EUSES, and the concentration in soil into AgriSim.

Contamination with PCBs from polluted soil

Mamontova et al. (2007) sampled and analysed pasture soil, spring milk and autumn milk from 15 farms in Irkutsk, Russia and obtained PCBs concentration data of each. Though the concentration in air was not measured, they claimed that the effect of the background air concentration was negligible because of the low regional background air concentration and a strong disequilibrium between PCBs levels in air and soil (Mamontova et al. 2007), unlike the McLachlan (1996) study. Therefore the concentration in pasture soil was used as the contamination source into the three models.

Contamination with PCBs from polluted air, surface and shallow soil

Batterman et al. (2009) sampled and analysed air, surface soil (0-0.5 cm depth), sub-surface soil (1-2 cm depth), and milk in industrialized and urban areas of KwaZulu-Natal, South Africa and obtained PCBs concentration data of each. The unique aspect of this study was that the concentration in surface soil and sub-surface soil was separately monitored. The surface PCB concentration was about 5 times higher than the sub-surface concentration. This difference was explained by the variability of organic carbon and the possibility of the difference of the atmospheric deposition over space and through time(Batterman et al.

2009). The concentration measured in the surface soil was used for the soil-air-shoot and soil particle-shoot pathway in AgriCom. The averaged concentration in between surface and sub-surface soil was for the soil-cow pathway, and the concentration in subsurface soil was used for the root uptake and the soil-root-shoot pathway in the three models.

Contamination with POPs from polluted air and soil at different altitudes of a mountain range

Shunthirasingham et al.(2013) sampled and analysed air, soil and milk at three different altitudes (500 m, 1310 m, and 2052 m) in the Swiss Alps for obtaining POPs concentration data of each. The samples were taken in the August-September period when grazing occurs at the different altitudes. To reproduce the different behaviour of POPs depending on altitude, the vapour pressure of the POPs at each altitude was simulated separately by EPI-Suite with the mean temperature in the August-September period of each altitude. The low pasture was located in Zurich, and thus the temperature of 16°C in August-September was adopted from MeteoSwiss (2014) to estimate the vapour pressure of the POPs there. The temperatures of the middle pasture and the high pasture were then estimated using the mean temperature lapse rate of 6.25°C/km in August-September derived from a study in Alps(Rolland 2003). These simulated vapour pressures and the concentration in air at each altitude were incorporated into AgriCom and EUSES. The concentration in soil and the measured soil organic carbon content at each altitude were entered into the three models.

4-3-3 Uncertainty and Sensitivity Analysis

The uncertainty of the modelled outcomes caused by the variability of environmental properties and the parameter sensitivity was determined by using the Monte Carlo spread sheet add-in, Crystal Ball (Oracle, CA)(Decisioneering 2006). The procedure of the analysis was described in detail in Takaki et al. (2014). The environmental parameter set for these assumptions and their CV (coefficient of variability) values are given in Table 4-2.

TABLE 4-2. Assumption Parameters and the Coefficient Variation (CV) for the Uncertainty Analysis

Assumption parameters	CV(%)	Reference
Soil parameters		

Soil organic carbon	200	(Luo & Yang, 2007)
Bulk soil density	15	(Mckone & Enoch, 2002)
Soil particle density	5	(Mckone & Enoch, 2002)
Air content of soil	30	(Mckone & Enoch, 2002)
Water content of soil	30	(Mckone & Enoch, 2002)
Plant parameters		
Root density	5	(Mckone & Enoch, 2002)
Shoot density	30	(Mckone & Enoch, 2002)
Water content of plant	15	(Rikken et al., 2001)
Lipid content of plant	50	(Rikken et al., 2001)
Transpiration stream flow rate	100	(Luo & Yang, 2007)
Growth rate constant	100	(Luo & Yang, 2007)
Correction coefficient for root and shoot	1	(Trapp & Matthies, 1995)
Shoot volume	40	(Mckone & Enoch, 2002)
Leaf surface area	40	(Mckone & Enoch, 2002)
g (conductance)	100	(Rikken et al., 2001)
Parameters related to volatilisation		
Boundary layer thickness	100	(Spencer et al., 1988)
Dilution velocity in air	40	(Mckone & Enoch, 2002)
Parameters related to aerosol deposition		
Surface of aerosol	100	(Bidleman, 1988)
Deposition velocity	100	(Rikken et al., 2001)
Parameters related to soil-particle deposition		
Fraction dry matter leaf	100	(Mckone & Enoch, 2002)
Parameters related to cattle ingestion		
Daily intake of organic matter	20	(National Research Council, 1987)
Fraction of soil ingestion	67	(Duarte-Davidson & Jones, 1996)

4-3-4 Goodness of Fit Statistics

Two goodness of fit tests were chosen for evaluating the accuracy of the models against the experimental data: the residual sum of squares (RSS) as an indication of absolute differences between observed and estimated values, the standard errors (S_e) for normalising the differences of sample numbers(Hendriks et al. 2007);

$$RSS = \sum_{i=1}^{N} (m_i - r_i)^2 \qquad (4\text{-}1)$$

$$S_e = \sqrt{\sum_{i=1}^{N}(m_i - r_i)^2 / (N - 1)} \quad (4\text{-}2)$$

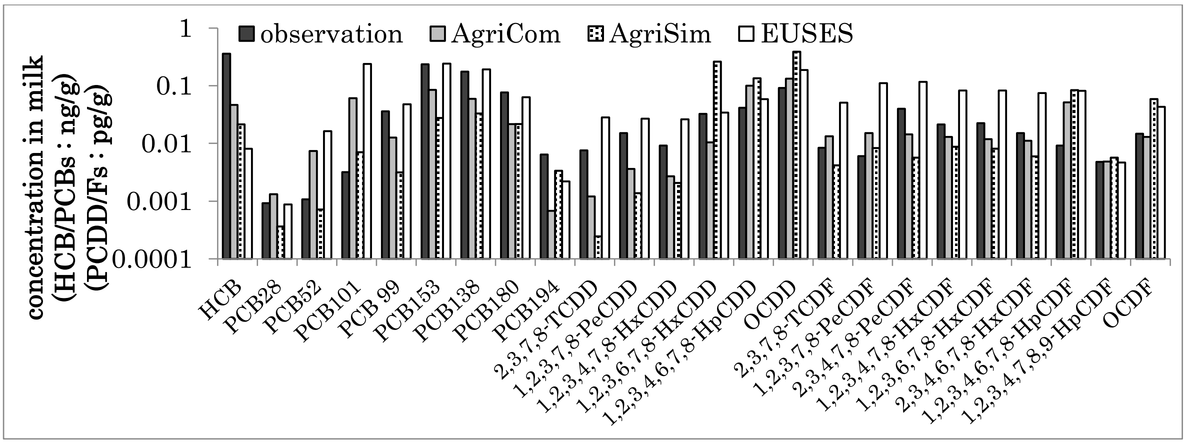
where N = sample number, m = simulated logarithm concentration in milk, r = observed logarithm concentration in milk.

4-4 Results and Discussion

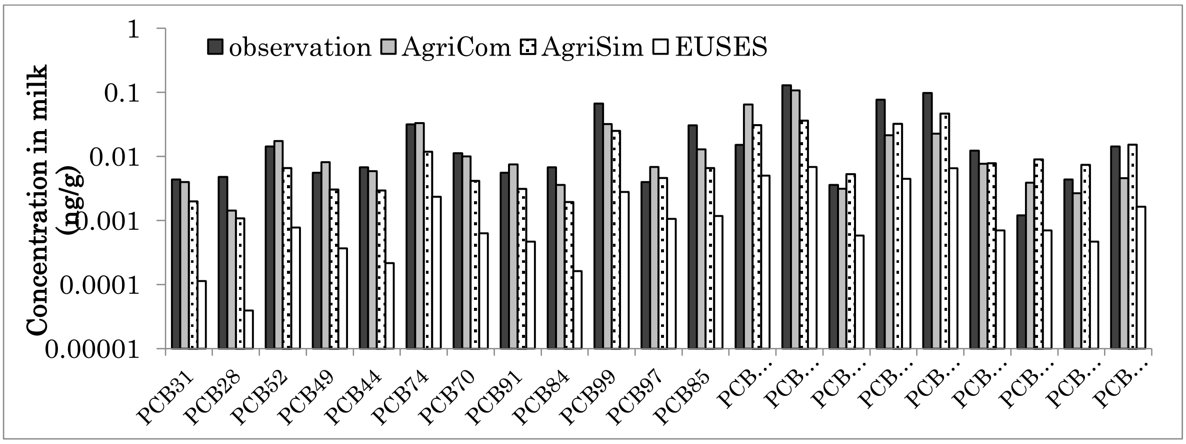
4-4-1 Scenario of Polluted Soil and Air

The model estimations of AgriCom, AgriSim, and EUSES compared against experimental observation for the concentration of hydrophobic pollutants in milk derived from polluted soil and air are shown in Figure 4-2a and 4-3a (McLachlan 1996). Each model reproduced the observed concentration in milk well but the goodness of fits test showed AgriCom was better than the others (S_e = 0.58 for AgriCom, 0.75 for AgriSim, and 0.76 for EUSES) (Table 4-3). When focusing on the estimation of each pollutant, only AgriCom did not underestimate over one order of magnitude. In terms of regulatory exposure assessment, model operators take underestimation more seriously to avoid false-negative decisions(Collins et al. 2006). AgriCom therefore presented a better performance in this case. In addition, HCB in milk mainly came via soil-air-shoot-cow pathway in the AgriCom simulation (Figure 4-4a) because of its higher K_{AW} and lower K_{OC} than those of other pollutants (US EPA 2012). It is suggested that this is the reason EUSES, which did not include that pathway, underestimated the HCB contamination. Figure 4-4a also showed that soil-cow pathway increased the contribution with increasing the number of chlorination and hydrophobicity.

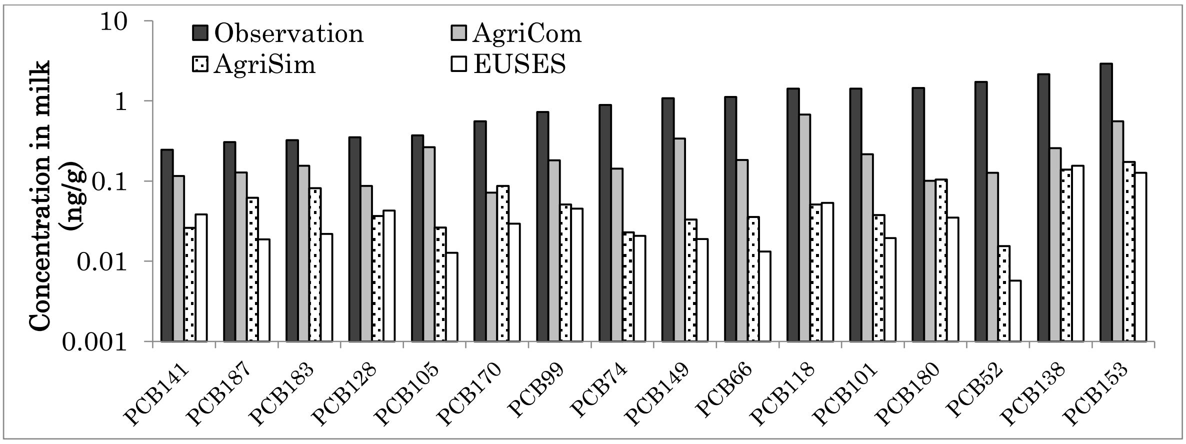
a) polluted soil and air scenario



b) polluted soil scenario



c) highly polluted soil surface scenario



d) different elevations scenario

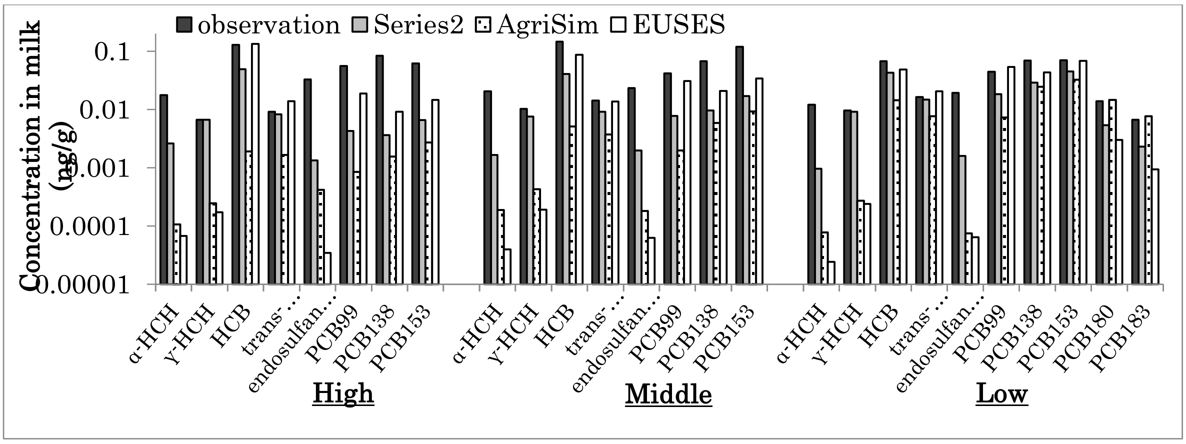
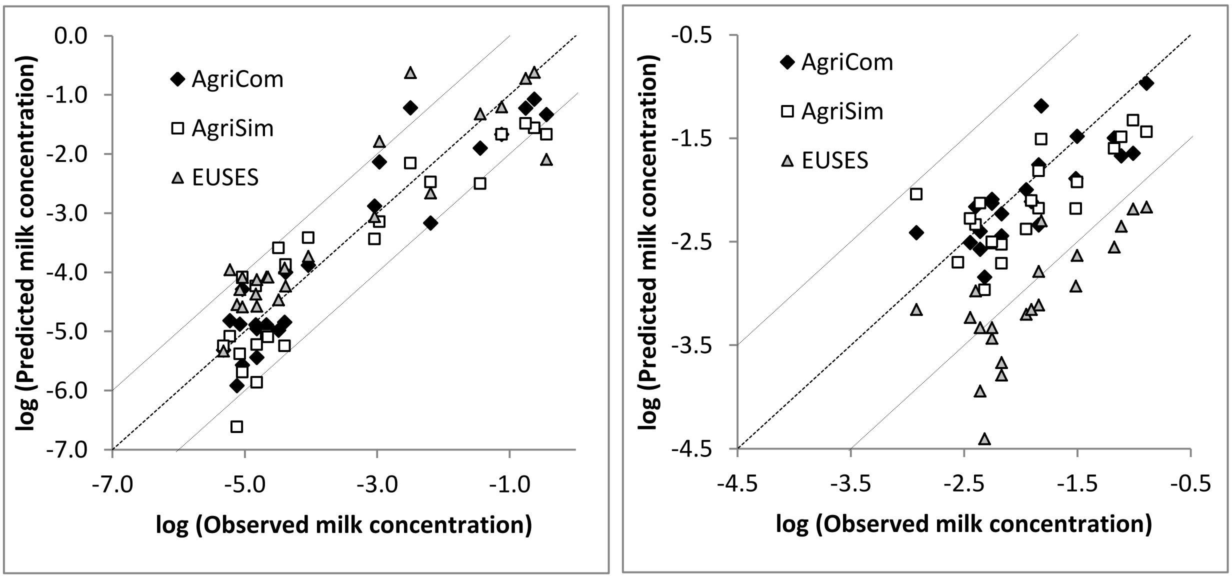
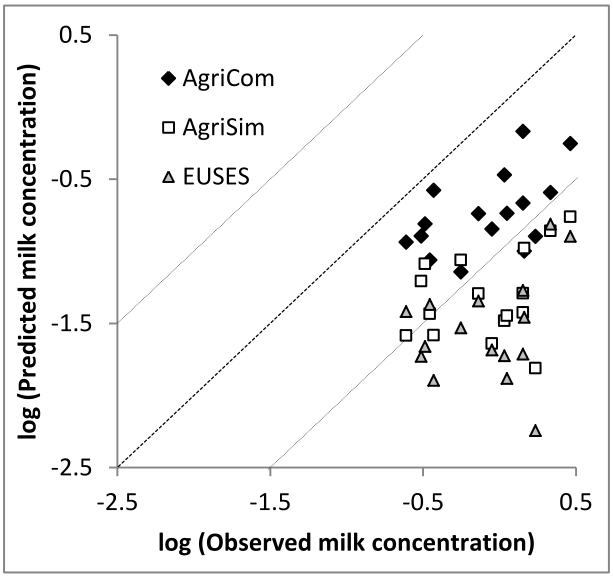


Figure 4-2 Observed and simulated POPs concentration in milk (black diamond: estimation by AgriCom, white square: by AgriSim, grey triangle: by EUSES) for four different scenarios: a) polluted soil and air scenario by McLachlan (1996), b) polluted soil scenario by Mamontova et al. (2007), c) highly polluted soil surface scenario by Batterman et al. (2009), d) different elevations scenario by Shunthirasingham et al. (2013)



a) polluted soil and air scenario b) polluted soil scenario

c) highly polluted soil surface scenario



d) different elevations scenario

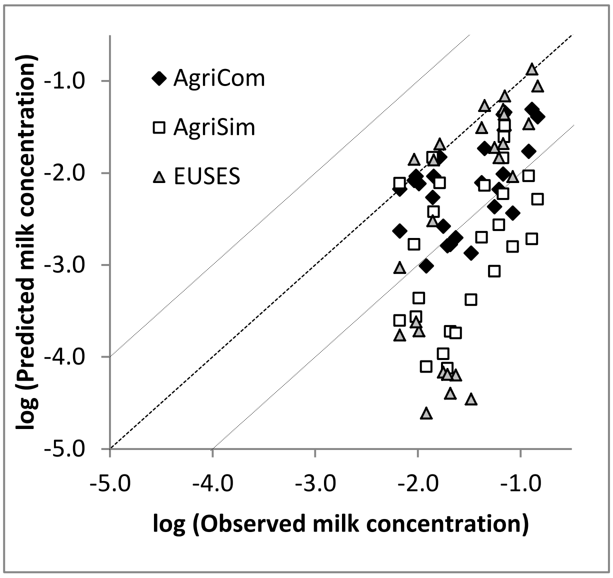
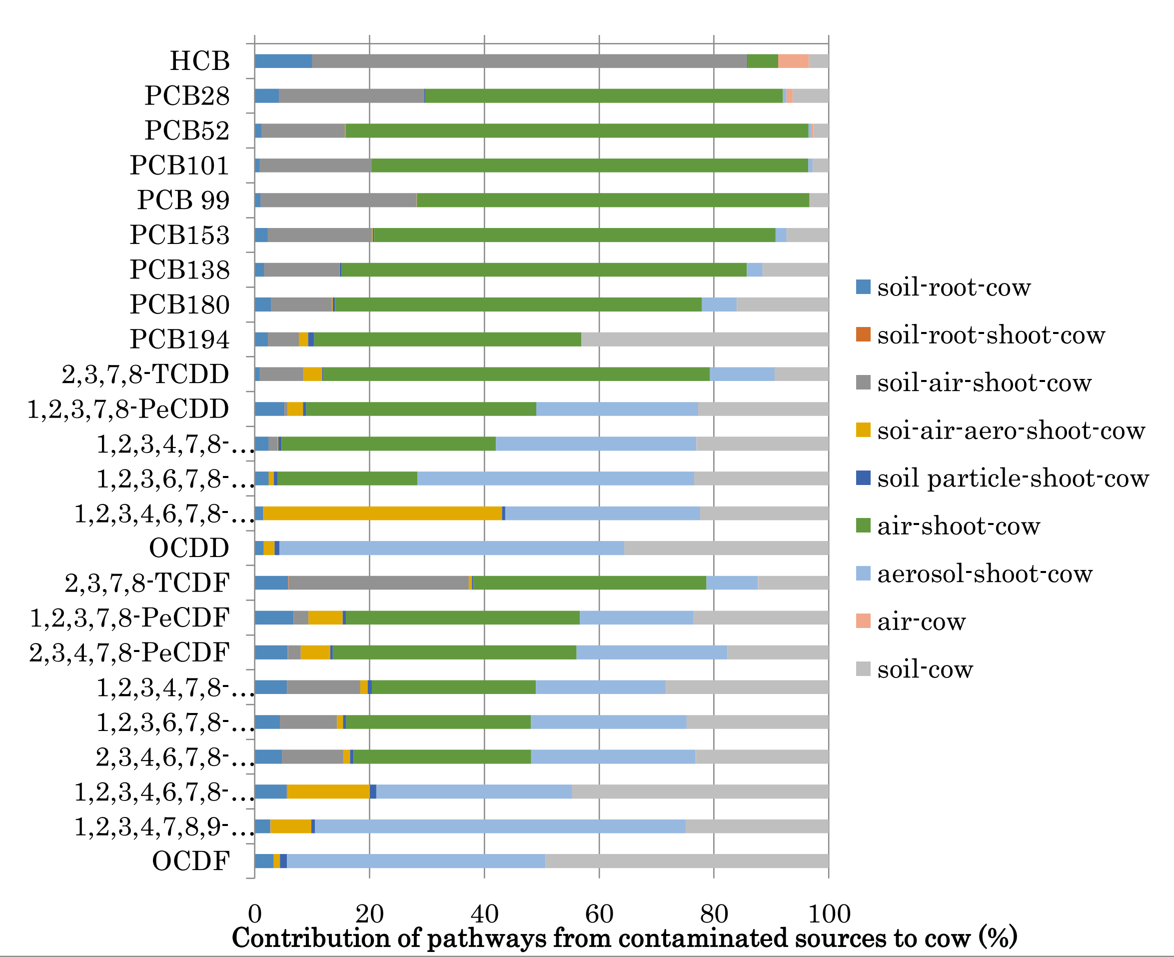
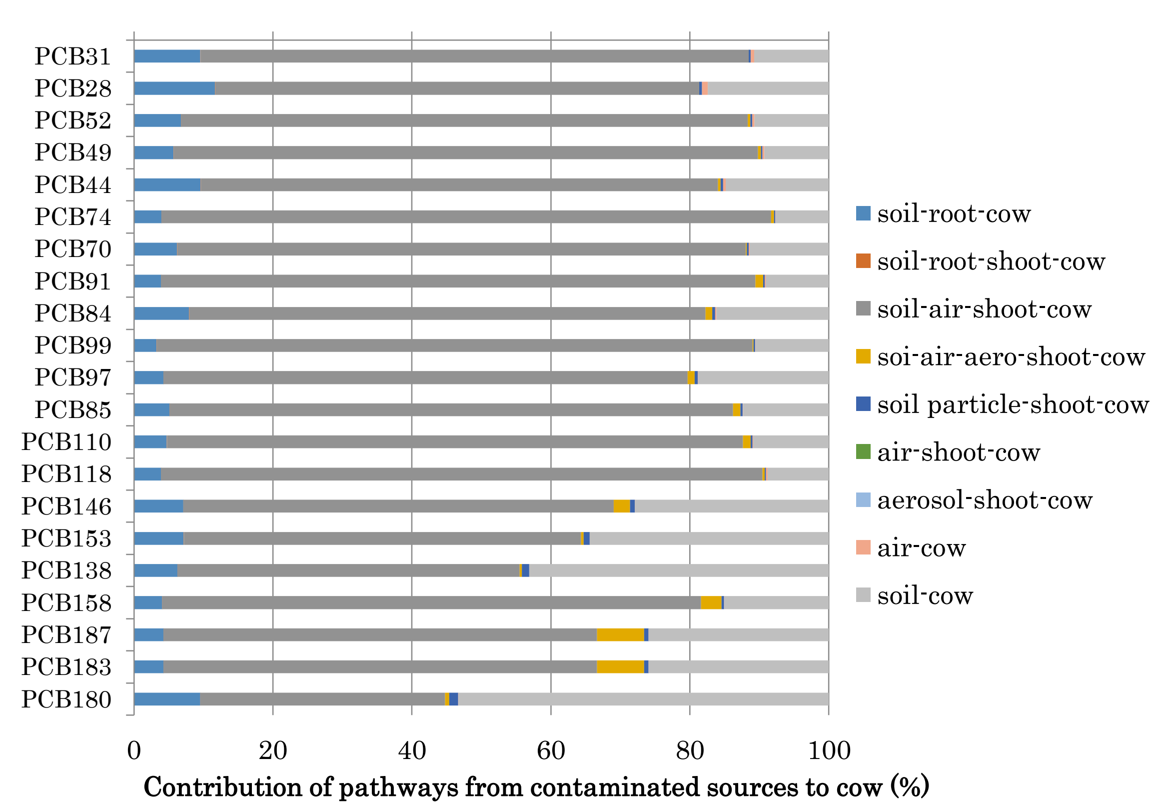


Figure 4-3 Observed and simulated POPs concentration in milk in Observed-Predicted chart (black diamond: estimation by AgriCom, white square: by AgriSim, grey triangle: by EUSES) for four different scenarios: a) polluted soil and air scenario by McLachlan (1996), b) polluted soil scenario by Mamontova et al. (2007), c) highly polluted soil surface scenario by Batterman et al. (2009), d) different elevations scenario by Shunthirasingham et al. (2013)

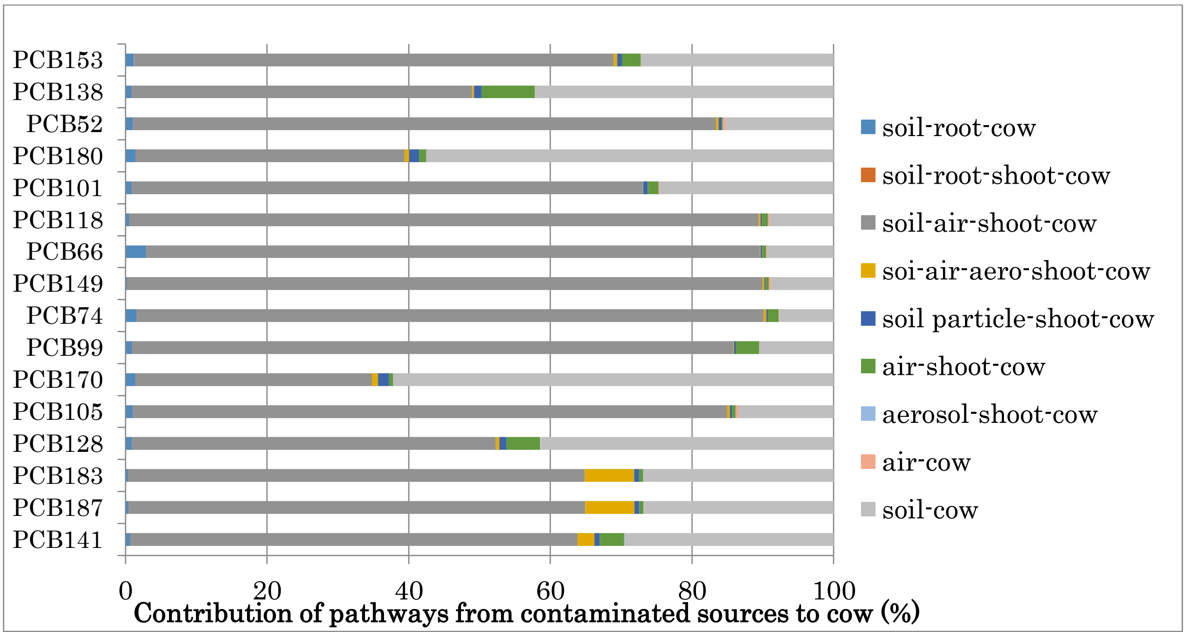
a) polluted soil and air scenario



b) polluted soil scenario



c) highly polluted soil surface scenario



d) different elevations scenario

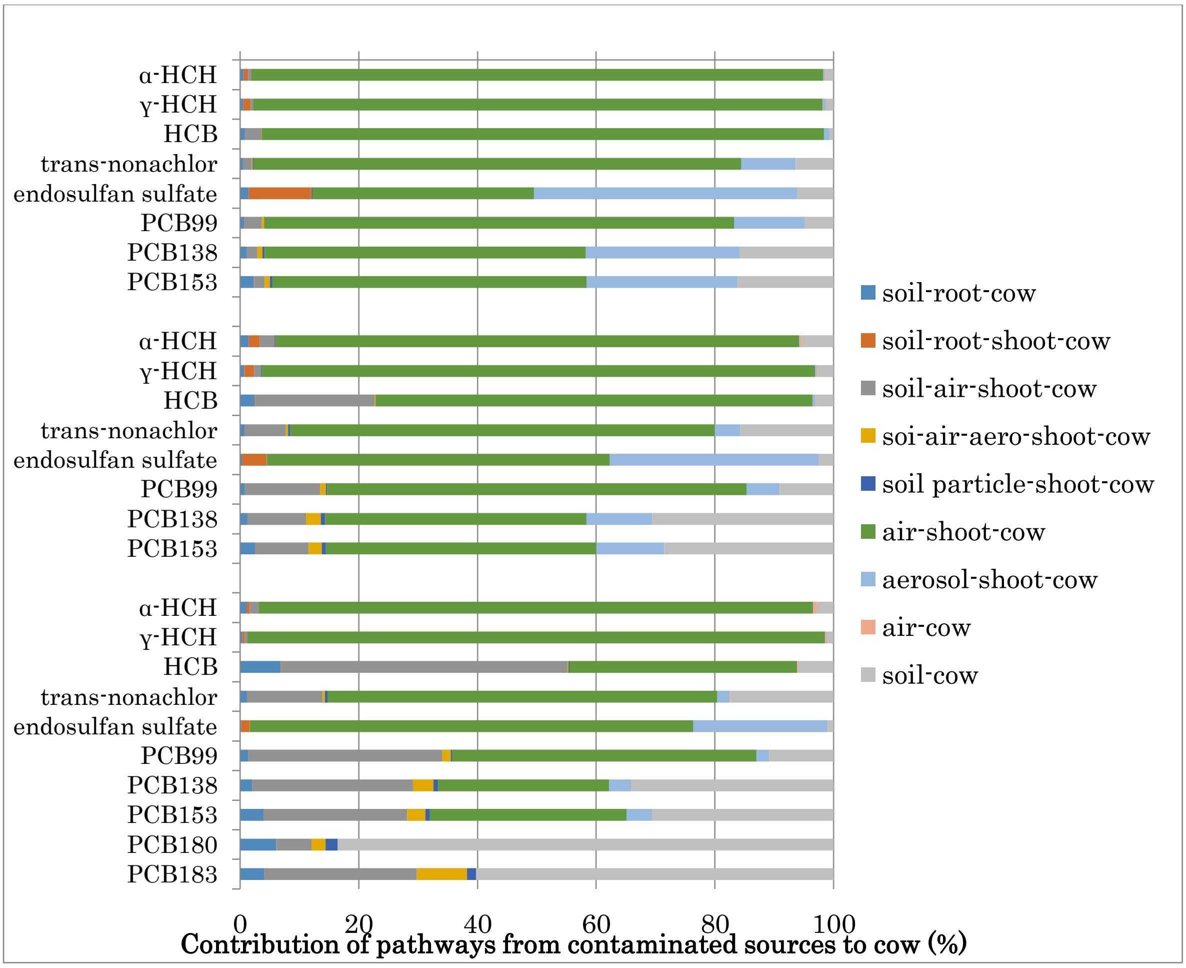


Figure 4-4 Contribution of each pathway from contaminated sources to cow in AgriCom for pollutants in four different scenarios: a) polluted soil and air scenario by McLachlan(Michael S. McLachlan, 1996)**, b) polluted soil scenario by Mamontova et al.(Mamontova et al., 2007), c) highly polluted soil surface scenario by Batterman et al.(Batterman et al., 2009), d) different elevations scenario by Shunthirasingham et al.(Shunthirasingham et al., 2013)**

TABLE 4-3. Goodness of fits between observed and simulated logarithm POPs concentration.

Models	n	Estimated versus Observed	
		RSS	S_e
a) Polluted soil and air scenario			
AgriCom	24	7.8	0.58
AgriSim	24	13.1	0.75
EUSES	24	13.3	0.76
b) Polluted soil scenario			
AgriCom	21	2.4	0.35
AgriSim	21	3.9	0.44
EUSES	21	31.8	1.26
b) Highly polluted soil surface scenario			
AgriCom	16	8.2	0.74
AgriSim	16	27.4	1.35
EUSES	16	36.5	1.56
AgriSim*	16	17.2	1.07
b) Different elevations scenario			
AgriCom	26	14.7	0.77
AgriSim	26	55.5	1.49
EUSES	26	53.6	1.46

Goodness of fit of the models is characterized by the residual sum of squares (*RSS*) and the standard errors (S_e).

*** the concentration in surface soil was used for shoot uptake**

4-4-2 Scenario of Polluted Soil

Model estimations were compared against experimental data of PCBs concentration in autumn milk produced with grazing on pasture from polluted soil (Figure 4-2b, 4-3b) (Mamontova et al. 2007). AgriCom and AgriSim reproduced the observed PCBs contamination in milk well (S_e = 0.35 for AgriCom, 0.44 for AgriSim) but EUSES showed severe underestimation (Se = 1.26) (Table 4-3). EUSES does not have soil-air-shoot and soil particle-shoot pathways for shoot uptake while the main contaminated source was soil in this scenario. It has been suggested that the soil-air-shoot pathway is dominant for shoot uptake for organic compounds with higher values of K_{AW} than 10^{-4} (Ryan et al. 1988; Duarte-Davidson and Jones 1996; Collins and Finnegan 2010; Undeman et al. 2009). All the PCBs in this scenario have the values of $K_{AW} > 10^{-4}$ (US EPA 2012), and AgriCom also simulated soil-air-shoot-cow pathway as dominant (Figure 4-4b). The lack of the soil-air-shoot pathway would thus lead to such an underestimation. AgriSim incorporated an empirical equation of plant uptake from soil to stem, namely, all the shoot uptake pathways including the soil-air-shoot are included in the empirical equation.

The standard errors of AgriCom and AgriSim in this scenario were smaller than those in the first scenario. This scenario has simpler exposure pathways with fewer contamination sources, only one category of the contaminants (PCBs), and the milk and soil were sampled on the same farm unlike in the first scenario.

4-4-3 Scenario of Highly Polluted Soil Surface

Model estimations were compared against observed PCBs concentrations in milk produced through grazing at a site with much higher concentrations at the surface than in the sub-soil (Figure 4-2c, 4-3c). AgriCom reproduced the observed milk contamination well while the other two models severely underestimated (S_e = 0.74 for AgriCom, 1.35 for AgriSim, 1.56 for EUSES, Table 4-3). Since the soil surface was highly polluted and the K_{AW} of all the PCBs was higher than 10^{-4}, the main pathway for shoot uptake was implied to be the soil-air-shoot and the AgriCom simulation supported this hypothesis (Figure 4-4c). The lack of the pathway within the EUSES model would therefore account for the underestimation of the milk concentration. The performance of AgriSim was improved when the concentration in surface soil was used instead of the concentration in soil below surface for shoot uptake (S_e = 1.07, Table 4-3). The simulated air concentration from volatilisation for AgriCom was about one order of magnitude higher than the observed air concentration. This implied that the air concentration near the ground where the pasture was exposed was higher than the background air concentration because of the volatilisation from highly polluted surface soil. This result indicated the importance of the surface soil concentration and following soil-air-shoot-cow pathway. Measuring and reducing the concentration particularly in surface soil was revealed to be important for the understanding of the contamination risk in milk exactly and the reduction of it.

4-4-4 Scenario of the Different Altitudes

The model estimations for each altitude were compared against experimental data (Figure 4-2d, 4-3d). AgriCom reproduced the observed concentration in milk better than AgriSim and EUSES; *RSS* for AgriCom was just around 28% of *RSS* for the other two models (Table 4-3).

At each of the three elevations, EUSES substantially underestimated for milk concentration of the three pollutants (α-HCH, γ-HCH, endosulfan sulfate), which were less hydrophobic than the others ($\log K_{OW}$ < 4). For estimating the cattle transfer EUSES incorporated a K_{OW}-regression, which estimates positive correlation between K_{OW} and the cattle transfer(Travis and Arms 1988), but the cattle transfer of an organic compound was reported to be correlated with the transformation rather than hydrophobicity(Hendriks et al. 2007). The consequence of this was that EUSES failed to estimate the cattle transfer for persistent and less hydrophobic compounds(Hendriks et al. 2007).

AgriSim generally underestimated the milk contamination, possibly because it lacks the air/aerosol-shoot-cow pathway, which was the main pathway for the majority of the pollutants according to AgriCom simulation (Figure 4-4d). When that pathway was not major in AgriCom simulation (PCBs at low altitude, Figure 4-4d), AgriSim reproduced the milk contamination well.

Adjusting vapour pressure for each altitude in AgriCom contributed to its good performance (*Se* : 0.77 for the adjusted vapour pressure, 1.07 for the non-adjusted vapour pressure(at 25°C)). AgriCom underestimated the milk contamination by more than one order of magnitude for endosulfan sulfate at every altitude, PCB99 and PCB138 at high altitude, and α-HCH at middle and low altitudes. The milk contamination of γ-HCH was reproduced well by AgriCom. This difference between the two optical isomers would appear to come from the different transfer factors into milk between the two. For example, the observed carry-over rate of α-HCH from pasture to milk has been reported 3-6 times higher than γ-HCH(McLachlan 1993). Introducing the observed transfer factor in milk of α-HCH improved the AgriCom estimation of the milk contamination (Figure 4-5).

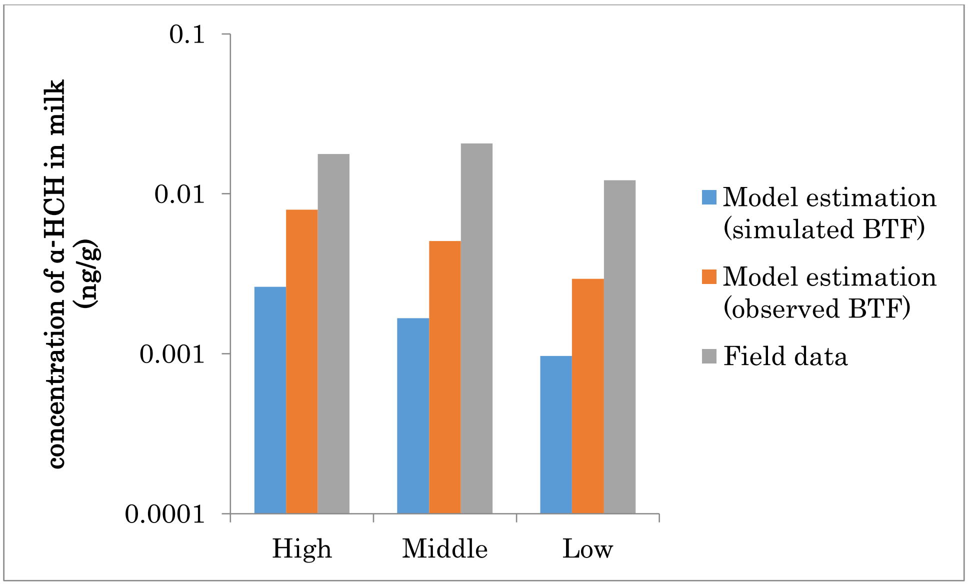
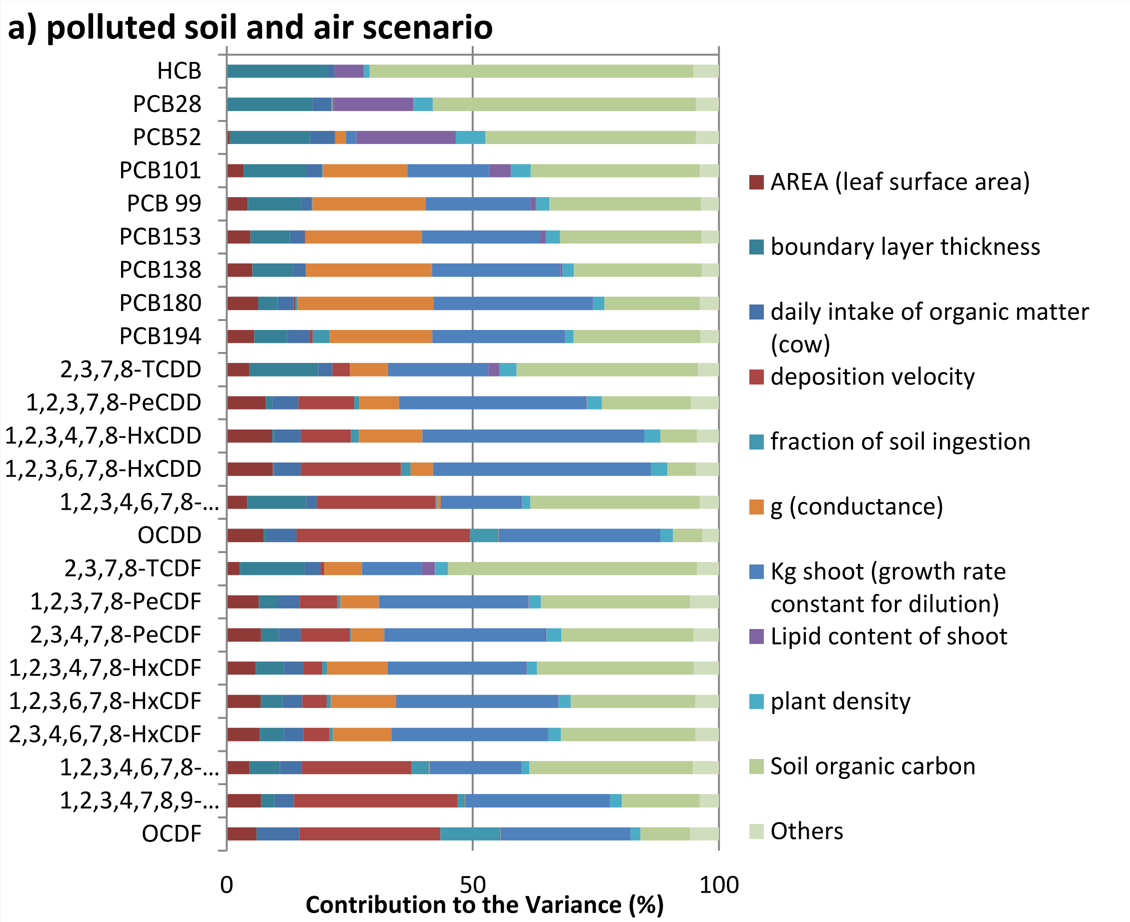
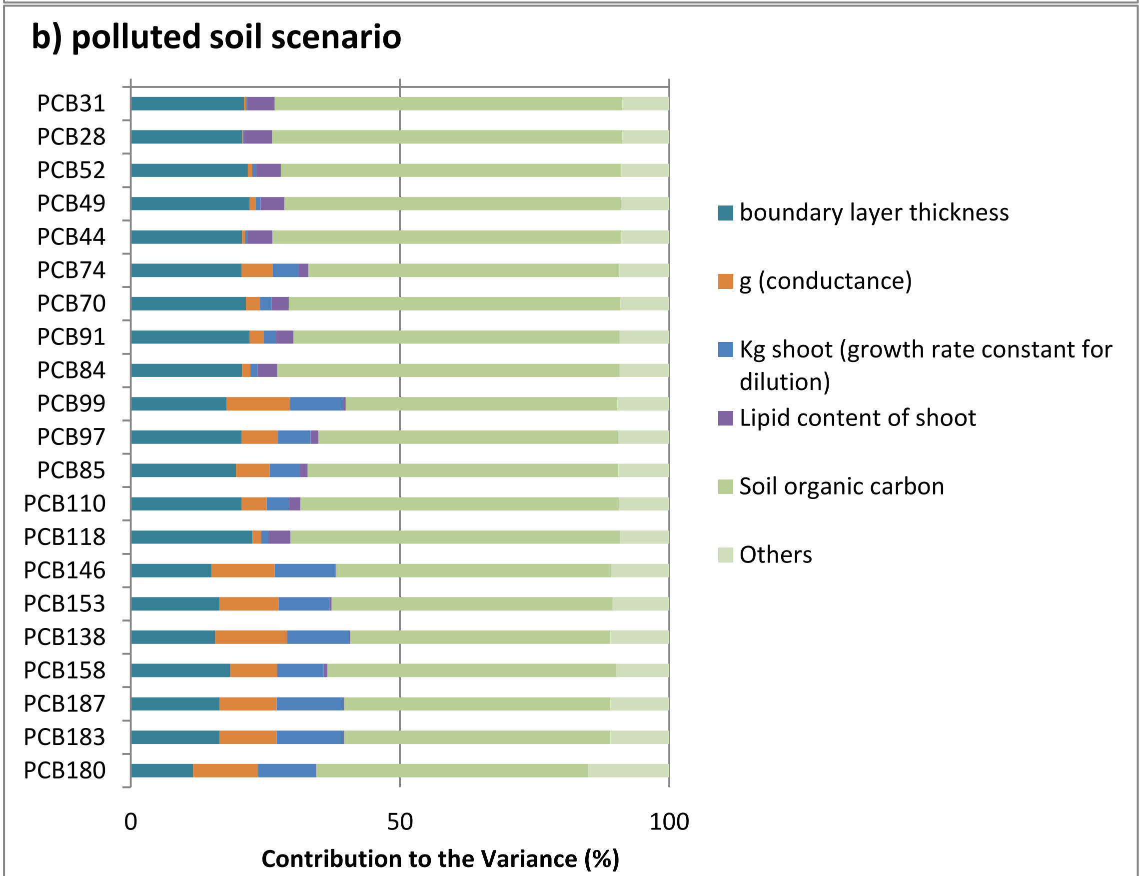


Figure 4-5 Observed and simulated concentration of α-HCH in milk in the different altitudes scenario. Two simulated concentration was expressed; one was estimated with using the simulated BTF of α-HCH and the other with using the observed BTF.

According to the sensitivity analysis, the shoot growth rate was the most sensitive parameter for endosulfan sulfate, PCB99 and PCB138, whose milk contaminations were underestimated particularly at high altitude (Figure 4-6). When optimising the growth rate of shoot for minimising the residual errors at each altitude, the performance was improved further (*Se*: 0.77 → 0.40) and the optimised growth rates at the high and middle altitudes were lower than that at the low altitude (0.0006 (high), 0.0005 (middle), 0.002 (low), day^{-1}). This result seemed reasonable because the lower temperature at the higher altitude could inhibit the grass growth. When considering the milk contamination at different altitudes, the grass growth could be as much important factor as the vapour pressure.


a) polluted soil and air scenario
HCB
PCB28
PCB52
PCB101
PCB 99
PCB153
PCB138
PCB180
PCB194
2,3,7,8-TCDD
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,4,6,7,8-...
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,6,7,8-...
1,2,3,4,7,8,9-...
OCDF
0
50
100
Contribution to the Variance (%)
AREA (leaf surface area)
boundary layer thickness
daily intake of organic matter (cow)
deposition velocity
fraction of soil ingestion
g (conductance)
Kg shoot (growth rate constant for dilution)
Lipid content of shoot
plant density
Soil organic carbon
Others


b) polluted soil scenario
PCB31
PCB28
PCB52
PCB49
PCB44
PCB74
PCB70
PCB91
PCB84
PCB99
PCB97
PCB85
PCB110
PCB118
PCB146
PCB153
PCB138
PCB158
PCB187
PCB183
PCB180
0
50
100
Contribution to the Variance (%)
boundary layer thickness
g (conductance)
Kg shoot (growth rate constant for dilution)
Lipid content of shoot
Soil organic carbon
Others

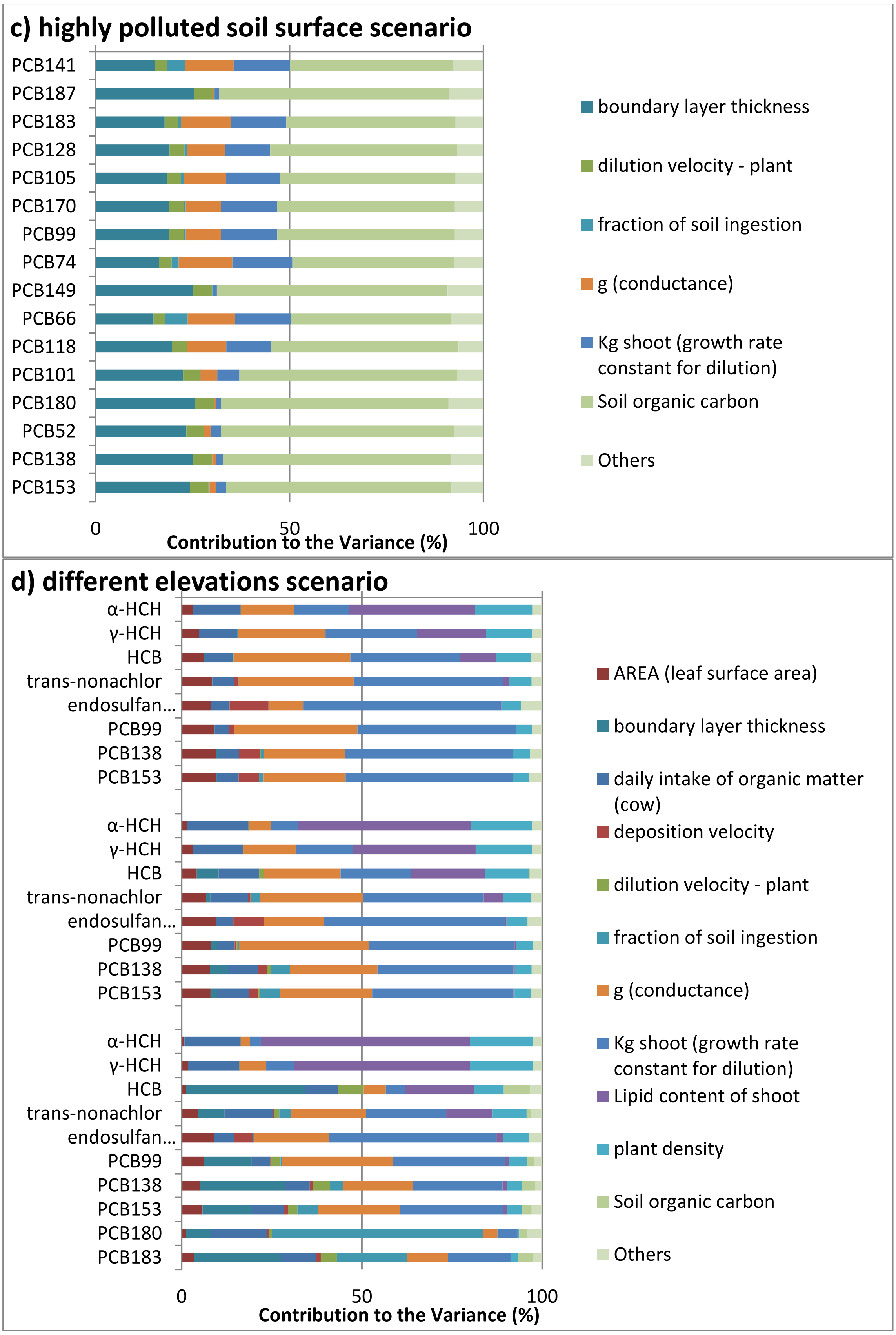


Figure 4-6 The results of sensitivity analysis for estimating milk concentration by AgriCom. The sensitivity of each parameter is described for the approximation of the contribution to the variance (%).

4-4-5 Uncertainty and sensitivity

Although AgriCom reproduced the observed concentrations of contaminants in milk for all the scenarios, the uncertainty analysis of the three scenarios of polluted soil and air, polluted soil, and highly polluted soil surface, showed high uncertainty of the model simulation; the averaged 90% confidence interval was up to two orders of magnitude (APPENDIX VI). The sensitivity analysis showed that the most sensitive parameter was soil organic carbon content for all the pollutants in the polluted soil scenario and highly polluted soil surface scenario, and for over 50% of the pollutants in the polluted soil and air scenario. Soil organic carbon content was particularly sensitive when the main contamination pathway was from soil via shoot in AgriCom simulation (Figure 4-6). Measuring the site specific value of soil organic carbon content would therefore be effective for reducing the model uncertainty and improving the performance. Since, in the different elevation scenario, the soil organic carbon content was measured at each elevation, the uncertainty was much smaller than the other scenarios, and the averaged 90% confidence interval was approximately one order of magnitude (APPENDIX VI). Shoot growth rate was the most sensitive parameter for over 60% of the pollutants in the different elevation scenario (Figure 4-6) and was particularly sensitive when the air/aerosol-shoot-cow pathway was dominant. The contribution of pathways was closely related to the identity of the sensitive parameter.

4-5 Conclusion

The outcomes from the four case studies showed that EUSES and AgriSim did not estimate milk concentration well in situations where the soil-air-shoot-cow and air/aerosol-shoot-cow pathways were dominant respectively due to the absence of the relevant pathway in each model. EUSES also did not reproduce the observed milk concentration of less hydrophobic POPs due to the limitation of the K_{OW} regression model of cattle transfer. Though EUSES and the Technical Guidance Document (European Commission 2003) were not developed originally for an assessment of contaminated soil, these are often used or referred to for assessing the risk of contaminated soil by regulatory agencies(Elert 2008; VKM 2009). These limitations in EUSES and TGD will produce inaccurate regulatory assessments. Two recommendations are made. The first is that the soil-air-shoot and ambient air-shoot pathway should be calculated separately. The second is that the K_{OW} regression of transfer factor to milk used in EUSES be replaced with the cattle biotransfer models using metabolic rate predicted by QSAR biodegradation models as is done in the AgriCom model. AgriCom satisfies these recommendations and showed the highest performance for all the scenarios. However, the disadvantage of AgriCom was its complexity since a simpler model with fewer model parameters is often preferable in regulatory risk assessment(Trapp and Schwartz 2000). The appropriate model selection will depend on the contamination scenario and the requirement of the assessment.

The uncertainty analysis demonstrated that the 90% confidence interval was often higher than two orders of magnitude, and soil organic carbon content contributed to the variance the most in AgriCom. Measuring a site specific value of soil organic carbon content is effective to reduce its uncertainty. This is a routine measure within the suite used for the evaluation of an agricultural soil.

The model performances of almost all components of AgriCom have been checked against experimental data of hydrophobic organic pollutants and the observed bioconcentrations and transfers of the pollutants have been reproduced well: soil-root crops (Takaki et al. 2014), soil-leafy crops (Takaki et al. 2014), air-leafy crops (C. D. Collins and Finnegan 2010), feed-cow milk (Takaki et al. 2015), feed-beef (Takaki et al. 2015), and soil/air-grass-cow milk (this study). This model is therefore recommended for adoption into regulatory risk assessment tools as a part of exposure assessment of agricultural food chains.